DTU Library

Removal of residues from reactive ion etched silicon surfaces characterized with XPS and Raman spectroscopy

Brøgger, Anna Line; Schmidt, Michael Stenbæk; Boisen, Anja

Published in:
Proceedings of the 40th International Conference on Micro and Nano Engineering

Publication date:
2014

Removal of residues from reactive ion etched silicon surfaces characterized with XPS and Raman spectroscopy

Anna Line Brøgger [a], Michael Stenbæk Schmidt [a], Anja Boisen [a]

[a] DTU Nanotech, Technical University of Denmark, Kgs. Lyngby, 2800, Denmark
e-mail: alibr@nanotech.dtu.dk

Keywords: RIE, SF_6, Raman spectroscopy, SERS, XPS, silicon nanopillars, SEM

It is known, that Reactive Ion Etching (RIE) processes have various negative effects on the electronic performance of silicon devices [1]. Detrimental RIE effects include lattice damage, diffusion of dopant ions and deposition of etching residues on the surface. Commonly efforts have been concentrated on removing the lattice damage since this seems to be the critical when fabricating MEMS devices. However, for other applications such as solar cells and sensing applications cleanness of the silicon surface is important.

Previously, Thomas *et al.* [2] characterized a silicon surface exposed to SF_6/O_2 RIE with X-ray Photoelectron Spectroscopy (XPS) and found that fluorine was left on the surface as a residue from RIE processes. Here, in this work, the effect of plasma ashing and thermal treatment in an effort to remove reactant residues from the surface of RIE processed silicon was studied by XPS and Surface Enhanced Raman Spectroscopy (SERS).

As an example of a RIE process we used a SF_6/O_2 RIE process to fabricate silicon nanopillars, cf. Schmidt *et al.* [3]. To test the hypothesis that the etchant residues can be removed from the surface by chemical reaction/sputtering and/or thermal desorption, the nanopillars were subsequently treated either/both with a standard O_2 plasma ashing for 1 min and/or placed in a furnace at 800 ^oC for 3 hours in a N_2 atmosphere. The surface of the nanopillars was characterized by XPS and the result is shown in Figure 1 and Table 1. XPS reveals that the surface contains a mixture of mostly silicon, carbon and oxygen and as expected, also fluorine as a residue from the RIE process. The surface is contaminated with approximately 5 atomic percent fluorine after the RIE process. This does not change upon O_2 plasma ashing. However, the fluorine is practically removed after the thermal treatment.

The silicon surface is also characterized using SERS and the results are shown in Figure 2. In order to perform SERS we create plasmonic structures by evaporating 225nm of silver onto the nanopillars after plasma/thermal treatment. SEM images of silver coated nanopillars without and with thermal treatment is shown in Figure 3 and Figure 4, respectively. It can be seen that the pillars do not change shape or form after the thermal treatment, and that the coverage of the silver coating is similar in both cases, making it suitable to compare the SERS measurements. The SERS substrate now created usually performs by trapping an analyte between the nanopillars enhancing the Raman signal of the analyte. A significant part of the Raman signal also stems from the silver cavity formed at the lower part of the silver cap on the silicon pillar. This plasmonic cavity mode gives a strong Raman response from the surface of the silicon pillar. Hence, this SERS substrate is sensitive enough to enhance the signal from any etch residues located on the surface of the silicon as well. This makes it excellent for analysis of the cleaning procedures. A 1µl drop of H_2O is positioned on the SERS substrate. H_2O does not give rise to a significant Raman shift with our measurement conditions. As the drop evaporates, the surface forces pull the pillars together forming clusters creating electromagnetic “hot spots” which greatly enhance the SERS signal. The signal is measured at 780nm with 0.5mW and 50X for 3x1sec. These results indicate that significant levels of etchant residues are removed from the silicon surface at 800 ^oC.

In conclusion, the standard plasma ashing procedure has no effect on the cleanness of the silicon substrate after the RIE process. On the other hand, the thermal treatment of 800 ^oC seems to remove the unwanted fluorine from the surface. These findings can be utilized in applications where the surface of the silicon is important, e.g. in the solar cell and chemical sensing industries.

[1] G.S. Oehrlein, Mater. Sci. Eng. B 4 (1989) 441.
[2] J.H. Thomas III, B. Singh, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 10 (1992) 3039.
[3] M.S. Schmidt, J. Hübner, A. Boisen, Adv. Mater. 24 (2012) OP11.

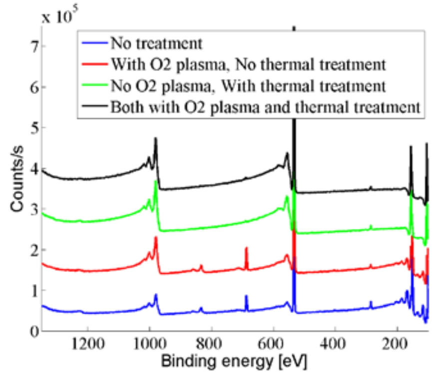

Figure 1. XPS results. The characteristic peak for fluorine is at 678 eV. The spectra are shifted for better visualization.

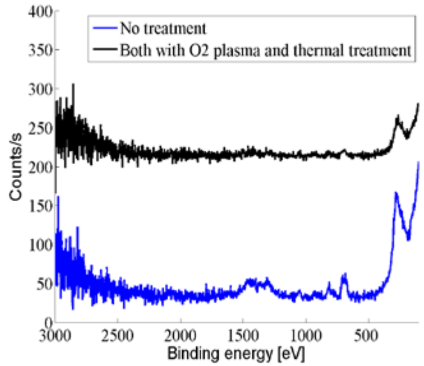

Figure 2. SERS results. The spectra are shifted for better visualization.

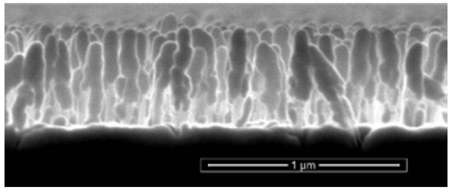

Figure 3. SEM figure of Ag coated Si nanopillars without thermal treatment.

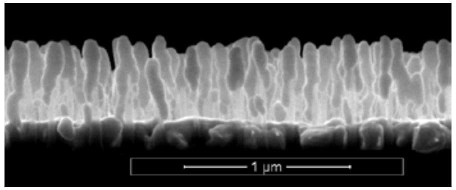

Figure 4. SEM figure of Ag coated Si nanopillars with thermal treatment.

Table 1. Results of the XPS analyzed by *Thermo Advantage v4.88.* The thermal treatment removes the fluorine from the surface of the sample.

At%	No O_2 plasma ashing No thermal treatment	O_2 plasma ashing No thermal treatment	No O_2 plasma ashing Thermal treatment	O_2 plasma ashing Thermal treatment
Oxygen	30.67	45.01	57.13	58.53
Silicon	54.67	44.72	38.95	37.90
Carbon	8.73	4.86	3.92	3.17
Fluorine	4.72	5.42	-	0.40
Nitrogen	1.22	-	-	-